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Short communication

A high power Sn–C/C–LiFePO₄ lithium ion batterySergio Brutti ^a, Jusef Hassoun ^{a,*}, Bruno Scrosati ^{a,*}, Chi-Yen Lin ^b, Han Wu ^b, Han-Wei Hsieh ^b^a Department of Chemistry, University of Rome Sapienza, 00185, Rome, Italy^b Advanced Lithium Electrochemistry, Aleees Group 33068, Taiwan, ROC

HIGHLIGHTS

- A high power lithium ion battery is here reported.
- The battery employs Sn–C anode and C–LiFePO₄ cathode.
- The battery operates with the high rate of 3C.
- A capacity of 130 mAh g⁻¹ is obtained with average voltage of 2.8 V.
- The system has low cost and high environmental compatibility.

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ABSTRACT

In this work we report a lithium ion battery characterized by very high rate capability, environmental compatibility, and potentially low cost. The battery is based on a lithium alloying, Sn–C, anode and an optimized lithium iron phosphate, LiFePO₄, cathode. The morphology and structure of the materials were characterized by using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques, while the electrochemical performances were evaluated by galvanostatic cycling and electrochemical impedance spectroscopy (EIS). Both the anode and the cathode reveal enhanced structure and morphology as well as excellent properties in terms of specific capacity, cycle life and, in particular, rate capability. The full Sn–C/LiFePO₄ lithium ion battery operates at 2.8 V with a stable capacity of about 120 mAh g⁻¹ for 100 cycles at the high rate of 3C. The cell has an energy density of 350 W h kg⁻¹ and a power density of 2.4 kW kg⁻¹. These interesting properties candidate the lithium ion battery here reported as a very appealing energy storage system, in particular for applications requiring high power densities.

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1. Introduction

Presently, hydrocarbon-fuelled cars powered by internal combustion engines dominate the road transportation market whereas electric or hybrid vehicles have only a marginal role [1]. The most promising candidates to boost the market share of electric vehicles (EV) are the lithium ion batteries in view of their high energy and power densities [2]. However, batteries with the conventional commercialized cell design, based on lithium cobalt oxide cathode and graphite anode [3], barely meet the EV transportation requirements and, consequently, improvements in terms of capacity and power are required. Furthermore, other factors

favouring the evolution of electric vehicles, such as cost, environmental compatibility, and safety, are as important as the performance of the powering battery. Therefore, breakthrough innovations in the formulation of Li-ion cells, in particular tailored for transportation, are in urgent need.

Olivine lithium iron phosphate (LiFePO₄) is a very popular cathode material due to its low cost, high environmental compatibility and improved safety [4]; many efforts have been devoted to optimize its battery performance by improving electronic conductivity, rate capability and lifetime [5,6]. In particular, proper carbon coating is of key importance for the improved performance as well as the widespread acceptance of the material [7–11]. On the anode side, very appealing candidates are lithium–silicon and lithium–tin alloys that are electrode materials having capacity far exceeding that of the conventional graphite electrodes, i.e. 4200 mAh g⁻¹ and 990 mAh g⁻¹, respectively, versus 372 mAh g⁻¹. The severe issue of volume changes experienced in the course of

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the lithium insertion–extraction electrochemical process [12] has been solved recently by developing nanostructured composite materials of optimized morphology [13,14].

In this paper we report a lithium ion battery exploiting the combination of a refined carbon-coated LiFePO₄ cathode and a nanostructured Sn–C anode. We show that this battery has a very promising behaviour.

2. Experimental

The Sn–C anode was prepared as described in previous papers [14] with a final Sn to C weight ratio of 40:60, respectively. The LiFePO₄ cathode material is a commercial product, Model A1100, of its LFP-NCO product line developed and manufactured by Advanced Lithium Electrochemistry (Aleees Taiwan) and characterized by a carbon content of about 5% in weight.

The anode and cathode electrode films were prepared by blending the active materials, super P carbon and polyvinylidene fluoride (PVdF 6020, Solvay Solef) in N-methyl-2-pyrrolidone (NMP, Aldrich); the slurry was then cast on copper (anode) and aluminium (cathode) foils, and finally dried overnight under vacuum at 110°C. The active material loading was about 2 mg cm⁻² for the Sn–C and 4 mg cm⁻² for the LiFePO₄ electrode. Prior to full lithium ion cell assembling, the Sn–C electrode was partially pre-lithiated by a surface treatment [15] by placing it in direct contact with a Li foil whetted by the ethylene carbonate (EC), dimethyl carbonate (DMC) 1:1 w:w, LiPF₆ 1 M electrolyte solution for 15 min under a 2 t cm⁻² pressure.

The X-ray spectra were collected by using a Rigaku D-max X-ray instrument equipped with a Cu-K α radiation source. The SEM and TEM images were obtained by using a JSM-7001F Scanning Electron Microscope integrated with EDX (Energy Dispersive X-rays) probe and a JEOL JEM-2110 transmission electron microscope.

The electrochemical impedance spectroscopy (EIS) test was carried out on a cell with the three-electrode configuration, where lithium metal was used as both the counter and reference electrodes. The measurements were done on a VersaSTAT MC (Princeton Applied Research) with amplitude of 10 mV in a frequency range of 100 kHz to 10 mHz. The galvanostatic cycling tests on lithium half-cells were carried out with a Maccor battery tester using Swagelok type cells prepared by coupling the electrode under test with a lithium foil counter electrode in an ethylene carbonate (EC), dimethyl carbonate (DMC) 1:1 w:w, LiPF₆ 1 M electrolyte solution (LP30, Merck battery grade), soaked in a glass fibre separator (Whatman). The cycling tests were performed at various C-rates in the 2.5–4 V versus Li voltage range. The full Sn–C/LiFePO₄ battery was evaluated by galvanostatic cycling with a Maccor battery tester in Swagelok type cells formed by coupling the pre-treated anode [15] with the cathode in the ethylene carbonate (EC), dimethyl carbonate (DMC) 1:1 w:w, LiPF₆ 1 M electrolyte solution (LP30, Merck battery grade) with a glass fibre separator (Whatman). The battery was cathode limited and was cycled at 3C rate (1C rate, based on the cathode weight, was 170 mA g⁻¹) in the 1.8–3.5 V voltage range.

3. Results and discussion

3.1. Cathode material

Fig. 1 shows the SEM and the TEM images of the LiFePO₄ electrode used in this work. The SEM images (A,B) evidence a morphology formed by micrometric, sphere-like, particles that assure high tap density to the electrode. The TEM images (C,D) show the carbon layer coated on the LiFePO₄ particles. The coating is continuous, has a thickness lower than 10 nm, and is homogeneous without any isolated carbon nanoparticles contamination.

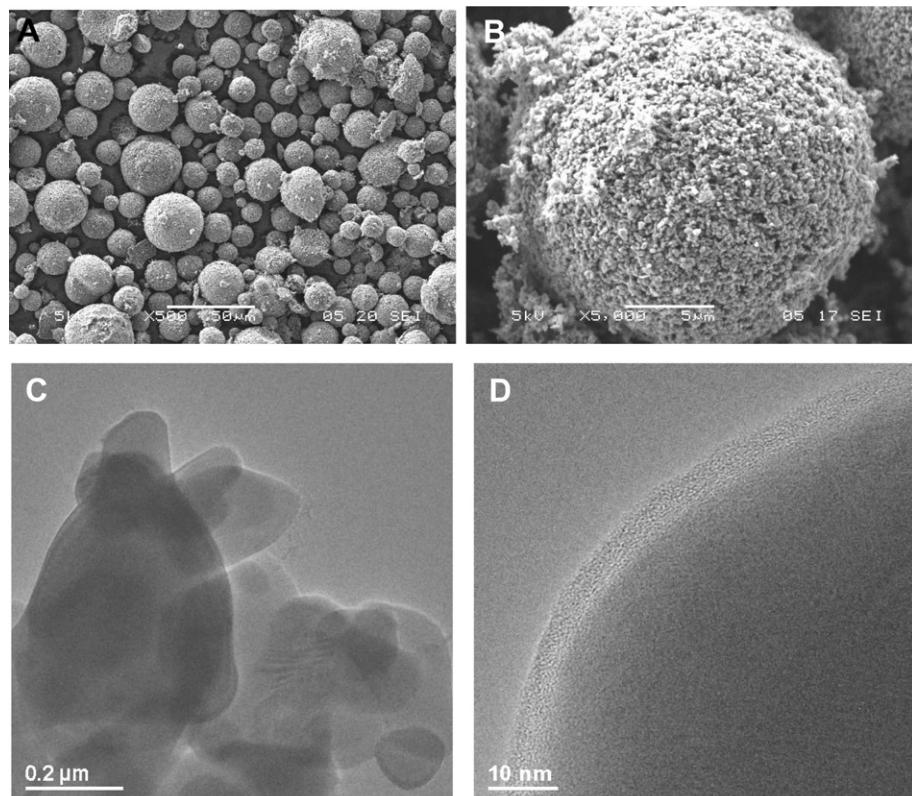


Fig. 1. (A,B) Scanning electron microscopy (SEM) and (C,D) transmission electron microscopy (TEM) images of the LiFePO₄ electrode reported in this work.

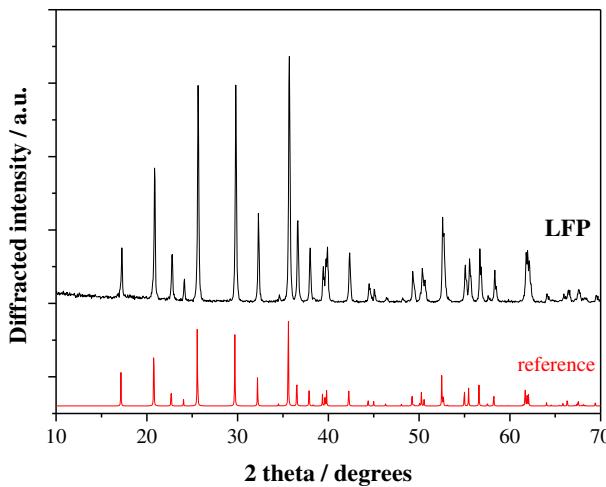


Fig. 2. X-ray diffraction (XRD) patterns of the LiFePO_4 electrode reported in this work.

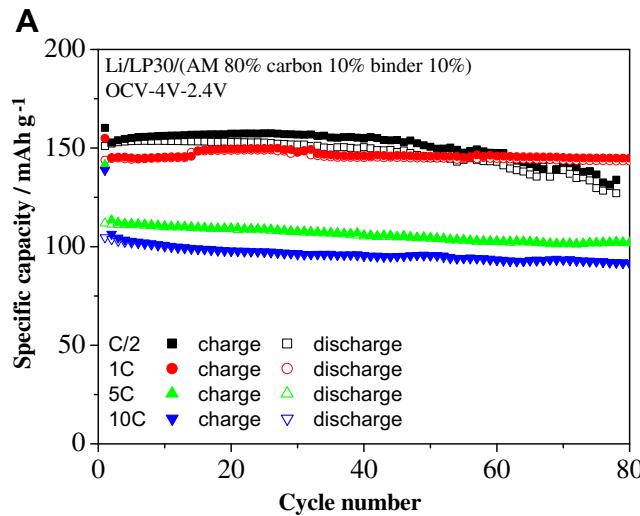


Fig. 3. Cyclic behaviour (A) and voltage profiles (B) of the LiFePO_4 electrode galvanostatically cycled at C/2, 1C, 5C and 10C rate in a lithium cell using ethylene carbonate (EC), dimethyl carbonate (DMC) 1:1 w:w, LiPF_6 1 M electrolyte solution. Room temperature.

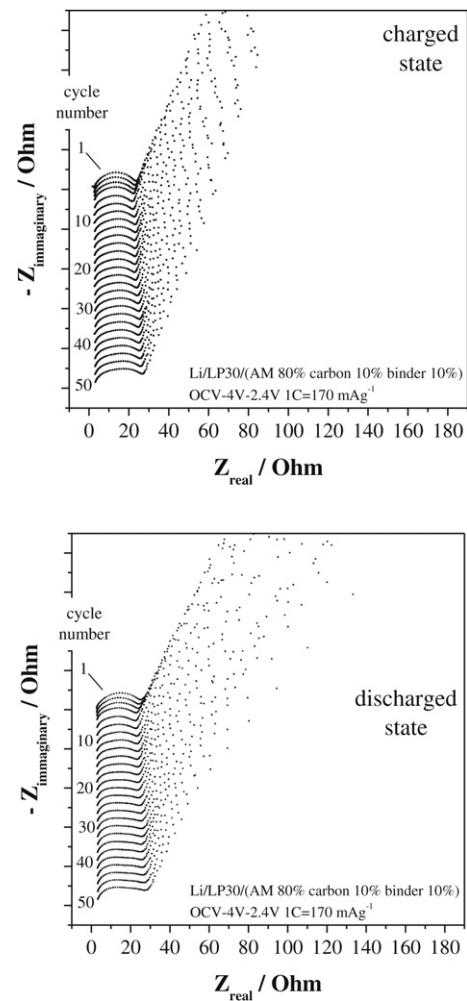


Fig. 4. Evolution of the impedance spectra upon galvanostatic cycling at C/2 of a LiFePO_4 lithium cell under fully charged and fully discharged states.

This refined coating morphology is expected to provide the electrode with an easy diffusion of the lithium ions and a very good electronic conductivity, which was indeed experimentally demonstrated, as mentioned in the paragraphs ahead.

Fig. 2 shows the X-Ray Diffraction (XRD) pattern of the C-coated LiFePO_4 electrode; a pure olivine structure (LiFePO_4 , JCPDS # 83-

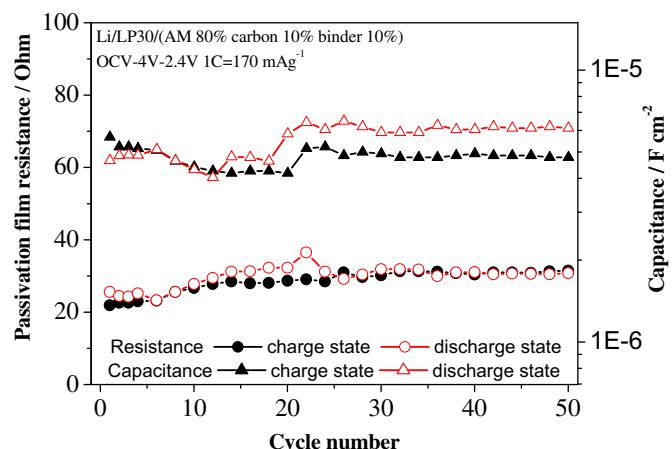


Fig. 5. Equivalent circuit data analysis calculated from the impedance spectra of a LiFePO_4 lithium cell galvanostatically cycled at C/2.

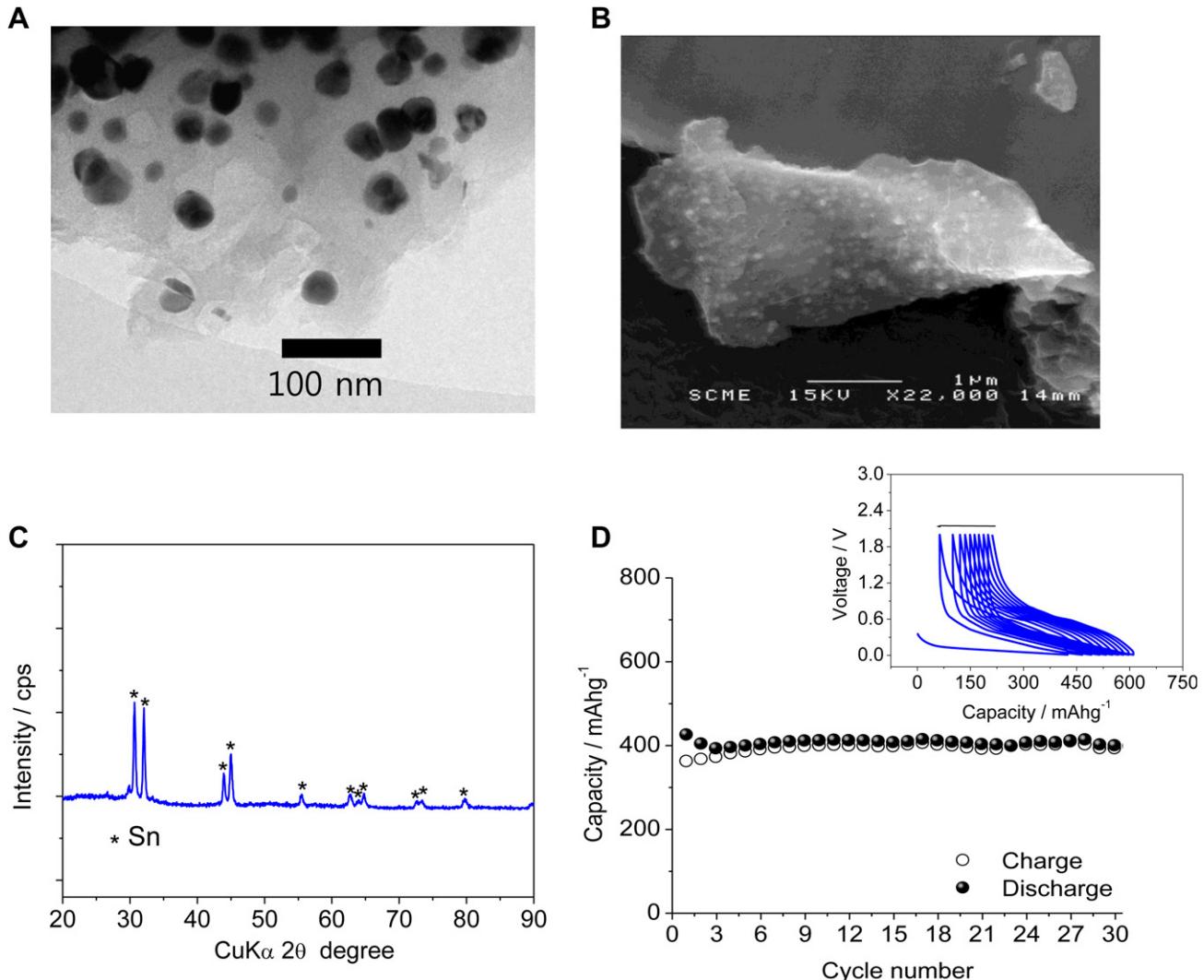


Fig. 6. (A) Scanning electron microscopy (SEM), (B) transmission electron microscopy (TEM) images, (C) X-ray diffraction patterns, and (D) behaviour in lithium cell cycled at 100 mA g^{-1} of the Sn–C electrode reported in this work.

2092) with no evidence of peaks associated with impurities, is revealed. A Rietveld refinement carried out by using the MAUD code [16] ($R_{wp} = 4.9\%$) suggests crystallites of about 94 nm in dimension and the following cell parameters: $a = 10.329 \text{ \AA}$, $b = 6.006 \text{ \AA}$, $c = 4.692 \text{ \AA}$, $V = 291.1 \text{ \AA}^3$. These values are in excellent agreement with the literature reference values ($a = 10.332 \text{ \AA}$, $b = 6.010 \text{ \AA}$, $c = 4.692 \text{ \AA}$ and $V = 291.4 \text{ \AA}^3$) [17]. The cation disorder (i.e. lithium ions randomly substituted by iron ions and vice versa) is estimated to be <0.1% in agreement with the very limited cell volume deviation between the calculated and the literature values.

The electrochemical response of the LiFePO₄ electrode has been first investigated in lithium half-cells. Fig. 3 shows the cyclic behaviour (A) and the voltage profiles (B) of the cells cycled at rates increasing from C/2 to 1C, 5C and finally, 10C. At the lower rates of C/2 and 1C the electrode has an excellent response, cycling with a capacity of about 150 mAh g^{-1} and with only a slight decay during cycles, in particular at C/2, due to the SEI film formation with electrolyte decomposition [18]. Even more impressive is the response at the high rates of 5C and 10C where a still notable capacity of about 100–110 mAh g^{-1} for over 80 cycles is provided. Such a good rate capability is clearly resulted from the refined coating morphology that provides the electrode of unique features in terms of electronic and ionic conductivity. In addition, the stable cycling response from

low to high rates also demonstrates that the carbon coating function is not altered even upon extended electrode operation.

Fig. 4 shows the Electrochemical Impedance Spectroscopy, EIS, response of the C-coated LiFePO₄ electrode taken under the fully charged and fully discharged conditions at progressive cycling stages. All the EIS spectra show a single semicircle feature. The mean capacitance value suggests that the semicircle can be attributed to the C-coating film on the electrode particle surface. However, convoluted semicircles with very small resistance values associated with the charge transference at the electrode interface are not excluded in the discharged state.

Both the capacitance and resistance values of this film are remarkably constant with only very limited variations upon cycling, see Fig. 5 that reports the ECS fitting data obtained by using an equivalent circuit of the R(RQ)Q circuit type.

3.2. Anode material

As to the anode material which couples with the C–LiFePO₄ cathode in view of a full lithium ion battery development, a tin–carbon, Sn–C nanocomposite [14] has been selected. Fig. 6 reports an overview of the properties and characteristics of this anode material showing its morphology by SEM (A) and TEM (B)

images, its phase structure by X-ray analysis (C), and its electrochemical response in a lithium half-cell in terms of cycling response (D). The morphology of this composite, with an overall crystalline structure, may be described as a series of tin nanoparticles uniformly dispersed in a micrometric carbon matrix. The reversible specific capacity during cycling (lithium–Sn alloying–de-alloying) of this material was measured to be in the order of 400 mAh g^{-1} .

3.3. Complete Li-ion cell

After having been characterized separately in lithium half-cells, the two electrode materials have been combined to form a complete Sn–C/C–LiFePO₄ lithium-ion battery using the standard ethylene carbonate (EC), dimethyl carbonate (DMC) 1:1 w:w, LiPF₆ 1 M electrolyte solution electrolyte. The expected overall electrochemical process of this battery is:

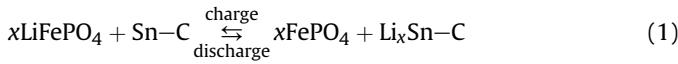


Fig. 7 shows the response of the battery when cycled at 3C in terms of voltage profiles (A) and capacity delivery (B). The battery operates along the expected 2.8 V level (see the half-cell data in Figs. 3B and 5D) delivering a reversible capacity in the order of 120 mAh g^{-1} in respect to the cathode active mass, i.e. versus LiFePO₄, with a steady-state charge-discharge efficiency approaching 100%. Slight capacity decay during cycling is observed in Fig. 7B, due to the above mentioned electrolyte decomposition with SEI formation, see discussion of Fig. 3.

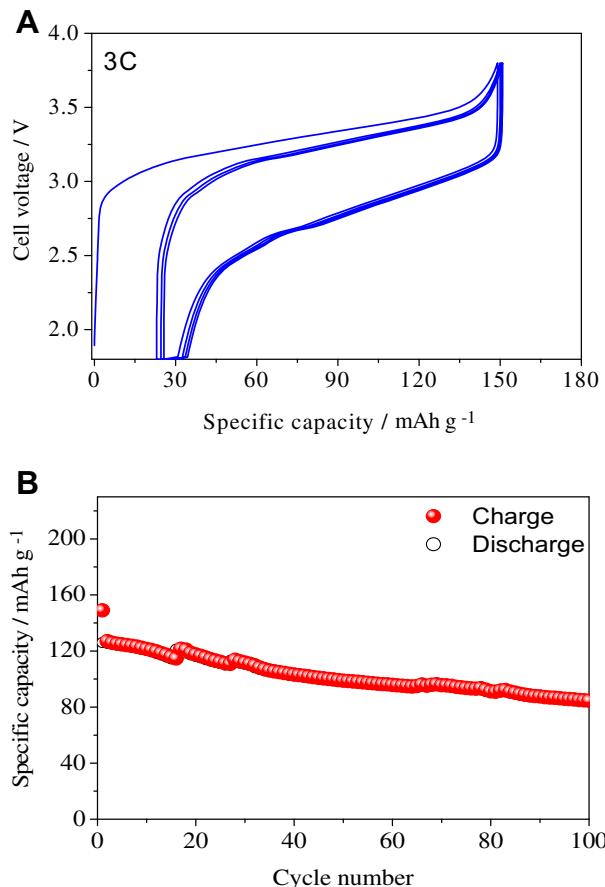


Fig. 7. Voltage versus specific capacity (A) and capacity versus cycles (B) profiles of the Sn–C/LiFePO₄ lithium ion battery galvanostatically cycled at a 3C rate using ethylene carbonate (EC), dimethyl carbonate (DMC) 1:1 w:w, LiPF₆ 1 M electrolyte solution. Room temperature.

This issue may be efficiently addressed by a proper electrolyte configuration as already demonstrated in our laboratory using a plasticized PEO-based electrolyte membrane, LiFePO₄ cathode and Sn–C anode in a solid cell characterized by good cycling stability [19]. The capacity and working voltage values of the cell give rise to a maximum specific energy and power density of 340 Wh kg^{-1} and of 2.4 kW kg^{-1} , (as calculated at a 5C rate) respectively. These values demonstrate that the Sn–C/C–LiFePO₄ lithium-ion battery here discussed has energy levels that are comparable to those of commercial counterpart systems. However, its safety and environmental compatibility levels are expected to be significantly better than the existing commercial systems.

4. Conclusion

We have shown in this work that, by combining a nanostructured Sn–C anode and a refined carbon-coated C–LiFePO₄ cathode, a new-design, high rate lithium ion battery can be composed. The charge–discharge tests demonstrated a good cycling response as the battery delivered a specific capacity of the order of 120 mAh g^{-1} at an average working voltage of 2.8 V. The data suggested values of energy and power densities of 350 Wh kg^{-1} and of 2.4 kW kg^{-1} , respectively, that compare well with those delivered by conventional lithium-ion batteries, but with intrinsic benefits in terms of expected safety, rate capability and environmental compatibility. Only a slight decay was observed after 100 cycle, probably due to some parasitic processes occurring at the electrodes. Some preliminary tests carried out on batteries having the same electrode couple but a different electrolyte (e.g., EC:DEC = 1:1 LiPF₆ 1 M instead of EC:DMC = 1:1 LiPF₆ 1 M) revealed that the decay in capacity can be mitigated by modifying the electrolyte formulation. In summary, due to the above stressed feature, we may conclude that the Sn–C/C–LiFePO₄ lithium-ion battery here reported may be considered as a very promising candidate for the development of new generation, efficient power sources for the electrified, sustainable road transportation.

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References

- H. Horie, T. Abe, T. Kinoshita, Y. Shimoida, World Electric Vehicle J. 2 (2008) 25.
- J.M. Tarascon, M. Armand, Nature 414 (2001) 359.
- B. Scrosati, J. Garche, J. Power Sources 195 (2010) 2419.
- F. Croce, A. D'Epifanio, J. Hassoun, A. Deptula, T. Olczak, B. Scrosati, Electrochem. Solid-State Lett. 5 (2002) A47.
- H. Huang, S.C. Yin, L.F. Nazar, Electrochem. Solid-State Lett. 4 (2001) A170.
- N. Ravet, Y. Chouinard, J.F. Magnan, S. Besner, M. Gauthier, M. Armand, J. Power Sources 97 (2001) 503.
- J. Ying, M. Lei, C. Jiang, C. Wan, X. He, J. Li, L. Wang, J. Ren, J. Power Sources 158 (2006) 543.
- L.N. Wang, Z.G. Zhang, K.L. Zhang, J. Power Sources 167 (2007) 200.
- K.-F. Hsu, S.-Y. Tsay, B.-J. Hwang, J. Mater. Chem. 14 (2004) 2690.
- T.-H. Teng, M.-R. Yang, S.-H. Wu, Y.-P. Chiang, K. Amine, Solid State Commun. 142 (2007) 389.
- S.-W. Oh, S.-T. Myung, S.-M. Oh, K.-H. Oh, K. Amine, B. Scrosati, Y.-K. Sun, Adv. Mater. 22 (2010) 4842.
- J.R. Dahn, R.E. Mar, A. Abouzeid, J. Electrochem. Soc. 153 (2006) A361.
- J. Hassoun, G. Mulas, S. Panero, B. Scrosati, Electrochim. Commun. 9 (2007) 2075.
- J. Hassoun, G. Derrien, S. Panero, B. Scrosati, Adv. Mater. 20 (2008) 3169.
- J. Hassoun, K.-S. Lee, Y.-K. Sun, B. Scrosati, J. Am. Chem. Soc. 133 (2011) 3139.
- L. Lutterotti, S. Matthes, H.-R. Wenk, Proceeding Twelfth Int. Conf. Textures Mater. (ICOTOM-12), vol. 1, 1999, p. 1599, <http://www.ing.uninett.it/~maud/>.
- V.A. Strel'tsov, E.L. Belokoneva, V.G. Tsirel'son, N.K. Hansen, Acta Crystallogr. B: Struct. Sci. 49 (1993) 147.
- D. Aurbach, J. Power Sources 89 (2000) 206.
- J. Hassoun, D.-J. Lee, Y.-K. Sun, B. Scrosati, Solid State Ionics 202 (2011) 36.